

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Conversion of Hydrocarbon Oils

We, ESSO RESEARCH AND ENGINEERING COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process and apparatus for converting hydrocarbon oils. It relates more particularly to a process and apparatus for the conversion of crude petroleum oil, wherein the feed is initially vaporized by contacting it with hot particulate solids and the solids so contacted, carrying a residual fraction of the feed, are further treated by coking. The invention has special application to whole crude oils but it is applicable also to topped crudes and other feeds which contain substantial proportions of lighter components in the gas oil boiling range, i.e., 430° to 1050° F.

The invention has particular application to the conversion of crude petroleum oil without the conventional initial atmospheric or vacuum distillation operation, although it can also be applied to a feed stock that has been topped by such an operation. By means of the present invention atmospheric stills and/or vacuum stills can be eliminated in many cases. In other cases the operational or quantitative requirement for such stills can be greatly reduced, i.e., they can be reduced in capacity.

The present invention involves combining the initial vaporization of an oil with the coking or upgrading of the heavy ends therefrom, the use of the coker vaporous products to assist vaporization, and the quenching of the vaporous coker products with the removal of heavy ends therefrom. This invention proposes a single vessel system for carrying out the combined vaporization and coking of an oil.

In the prior art, it has been customary to remove the lighter constituents of an oil, e.g., naphthas and gas oils, by distilling the oil and leaving a residuum or bottoms fraction of low value. In the past, atmospheric fractionators

and vacuum distillation units have been used to remove these lighter fractions. According to the present invention, an oil can be vaporized to secure an equivalent separation by contacting the oil with finely divided solids maintained at a suitable temperature. The lighter constituents of the oil are vaporized and separated and the heavier higher boiling constituents of the oil are deposited on the solids and removed along with the solids from the vaporization zone. The liquid portion of the oil on the solids is then coked or pyrolytically converted in a coking zone maintained at a suitable coking temperature.

Any relatively inert, preferably noncatalytic, solid of suitable particle size can be used in the practice of this invention if it has good heat transfer properties. Suitable particulate material may be sand, clay, spent catalyst, metal shot, glass or ceramic beads. Preferably, however, coke particles produced by the process having a size within the range of about 40 to 800 microns are used. The use of these coke particles makes it unnecessary to use extraneous solid materials as heat transfer media.

In conventional coking operations, wherein coking of a residuum is carried out in a coil, or a coil and drum apparatus, the conventional prolonged heating of the residuum to a temperature as high as 900° up to 1100° F. or more results in overcracking. The vaporized products, as well as the unvaporized products tend to be low in quality. Excessive amounts of coke are usually formed and deposited in the apparatus so that the coil and other apparatus elements become clogged. However, in a flash zone or vaporizer operated according to the present invention, and in the fluidized coking bed to which the residua are taken, no clogging of apparatus takes place and the overhead products are not degraded nearly to the same extent. The overhead products from the flashing zone (where they are contacted with the hot solids at 650° to 850° F.) are still of relatively good quality because of the short time duration of the treatment. Other things being equal, this means that they are better catalytic cracking feed stocks than gas oils

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from conventional coking. They are not subject to excessive degradation to coke or to excessive production of gases (below C₄) during the catalytic cracking operation which follows.

In brief compass, this invention proposes a hydrocarbon oil conversion process which comprises contacting an oil in an upper portion of a conversion zone with fluidized particulate substantially inert solids maintained at a temperature in the range of 650° to 850° F. to vaporize the lighter portions of the oil, removing overhead vapour and some solids with adhering unvaporized oil, separating the vapors as products, conveying the solids so separated along with adhering unvaporized portions of the oil to the lower portion of the conversion zone and maintaining in the lower portion fluidized particulate solids at a coking temperature in the range of about 900° to 1050° F. to convert the remainder of the oil pyrolytically to gasiform conversion products and carbonaceous residue which is deposited on the solids. The conversion products in the lower zone are passed upwardly to the upper portion to fluidize the solids therein and to assist in the vaporization of the oil. Because the upper portion operates at a lower temperature, the gasiform coking products are cooled in the upper zone and the heavy ends of the coking products are also condensed on the solids, and returned with the solids to the coking zone. Stripped solids are circulated from the lower portion of the coking zone to the upper portion or vaporization zone to maintain the vaporization temperature. The ratio of solids circulated to fresh feed is maintained sufficiently high so that the liquid deposited on the solids do not make the particles sufficiently tacky to adhere or agglomerate and cause bogging, i.e., the bed is kept relatively dry by an adequate solids feed rate. Solids are circulated from the lower portion to an external heating zone, e.g., a combustion zone, and back to maintain the coking temperature. The products from the process of this invention may be subjected to further processing either integral with or separate from the process. Thus the naphthas and/or gas oils may be reformed, desulfurized, catalytically cracked stabilized or blended.

In the drawing, annexed to and forming a part of this specification, there is shown diagrammatically an apparatus and a processing sequence operated in accordance with the teaching of this invention. It is to be understood that this drawing is merely exemplary and the invention is not to be limited thereto.

Charging stocks suitable for use in the present invention comprise, preferably, whole crudes and particularly crudes of a character that make it desirable to obtain only relatively low end point products therefrom. However, topped or partially topped crudes or residua may be also processed by this invention. The

invention is not to be limited to petroleum oils as it may find use in treating other hydrocarbons such as shale oils, coal tars or synthetic oils.

Referring to the drawing, a whole crude is introduced into the upper portion of a conversion or coking vessel 1 by line 2. This oil may be suitably preheated as by heat exchange with various product streams. The conversion vessel consists of two, upper and lower, portions or sections. The bottom section is designed to operate in a manner of a conventional downflow coker and is used to convert the heavy residual bottoms in the crude by pyrolysis. The top section is relatively small and operates in the manner of an upflow type fluid reactor. The zones are separated by a perforated plate 3 or the equivalent, such as grids, screens or packing that permits the passage of vapors while preventing backflow of the solids. The lower zone operates at a temperature of about 900° to 1050° F. and the upper zone operates at a somewhat lower temperature in the range of 650° to 850° F. Conventional fluidization gas velocities in the range of 0.2 to 5 ft./sec. are used in the lower coking zone and somewhat higher superficial vapor velocities in the range of 4 to 20 ft./sec. are used in the upper vaporization zone.

The upper section serves three purposes: (1) the light components of the feed are vaporized, and because of the low temperatures and high velocities, are quickly removed thereby avoiding undue degradation of the virgin feed; (2) the heavy high boiling ends of the oil are deposited on the coke; and (3) the coker vapors from the lower coking zone are quenched thereby preventing after-cracking, and the heavy ends of the vapors are also removed and deposited on the coke.

The liquid containing coke particles and the vapors are conveyed from the upper zone by line 4 to a separation system, e.g., a cyclone 5. The vapors are taken off overhead from the cyclone and are then conveyed by line 7 to a separation system 8. In some applications, it will be advantageous to immediately quench the vapors from the cyclone to a temperature below about 600° F. Cooled recycled oil streams can be used to accomplish this. As shown, a simple separation is made. Materials boiling above about 950° to 1050° F. are separated from the vapors and the vapors are sent to further processing by line 9.

The higher boiling material separated from the vapors, which contains any coke particles not removed from the vapors by the cyclone, is conveyed to the lower portion of the conversion vessel by line 11. If desired, a portion of the condensed material can be removed from the process by line 12 as product. This will prevent buildup of contaminants and unduly refractory constituents in the recycled material.

The solids removed from the vapors in cyclone 5, along with adhering liquid, are

transferred by line 13 to the lower portion or coking zone of the conversion vessel. In the lower zone, the liquid adhering to the solids is exposed to coking temperatures and undergoes
 5 pyrolysis. The evolved vapors pass upwardly through the vaporization zone as previously described. A stripping and fluidization gas, e.g., steam, is admitted by line 14 to the lower portion of the conversion vessel to first strip
 10 and then fluidize the solids in the coking zone.

Steam in amounts of 1 to 20 wt. % based on fresh feed can be used.

Stripped solids are circulated from the lower portion of the conversion vessel to the vaporization zone via line 15. These solids may be cooled in heat exchanger 16 as they are at a higher temperature than that existing in the upper zone. This heat exchange may be by
 15 any one of several well known means, e.g., steam may be generated for use in the process or for other purposes. A portion of the oil introduced into the upper zone may be mixed with these solids via line 2a prior to their entry into the upper vaporization zone. In this way,
 20 better dispersion of the oil and solids is obtained. The amount of solids circulated from the lower to the upper zone will amount to about 5 to 50 lbs./lb. of fresh oil. A relatively high solids to oil ratio is used so as to prevent
 30 agglomeration of the particles. This high solids to oil ratio coupled with the high vapor velocities is sufficient to obtain good operability.

To supply heat to the process, stripped coke is circulated from the lower zone to an external
 35 heating zone by line 17. Any heating means may be used including gravitating bed combustion units, fluid bed burners, shot heating systems, and other direct and indirect heating means. As shown, the solids are passed through
 40 a transfer line burner wherein a portion of the solids is combusted and the solids are heated to a temperature 100° to 300° F. above the coking temperature. A free oxygen-containing gas, e.g., air, is admitted to the base of a sub-
 45 stantially vertical transfer line burner and con-

veys the coke particles upwardly through the burner at velocities above 10 ft./sec., e.g., 60 ft./sec. This air will amount to about 200 to 800 cu. ft./lb. of fresh oil feed. The reheated solids are separated from the flue gases in
 50 cyclone 20, the flue gases being removed overhead from cyclone and vented via line 21. A portion of the heated solids is then circulated by line 22 to the solids outlet line of cyclone 5 and heats the solids in line 13 to prevent
 55 agglomeration of the solids. Another portion of the heated solids is transferred by line 23 to the coking zone. The amount of solids circulated from the coking zone and back usually amounts to 1 to 10 lbs./lb. of fresh oil feed. 60

In transfer line burner operations, it is advantageous to recycle some of the reheated solids to the burner inlet in order that a high initial combustion temperature may be maintained. This permits burners of shorter length
 65 to be used. Thus, a portion of the reheated solids are recycled to the burner inlet by line 24.

Under proper conditions, the process can be made to operate so that no excess coke will be
 70 produced, i.e., all the coke or carbonaceous residue formed by the process is combusted to supply the heat of vaporization and pyrolysis. If excess coke is produced, it can be removed by line 25. Extraneous fuel may be
 75 admitted to the burner by line 26, if it be desired, to be preferentially burned therein to heat the particulate solids.

The recycled oil from separator 8 may be introduced either into the upper or lower zone. 80 Preferably this oil is introduced into the lower portion of the lower zone as indicated. Being relatively volatile, it will vaporize readily and will replace or supplement the fluidization gas supplied by line 14. 85

To make the invention clear, a summary of the range of operating conditions pertinent to the present invention and a specific example are presented in Table I.

TABLE I.

		Range	Example
	Pressure, coker outlet, psi. - - -	0 to 400	6
	Temperature, ° F.		
5	Vaporization zone - - -	650 to 850	800
	Coking zone - - -	900 to 1050	950
	Average solids residence time, mins.		
	Vaporization zone - - -	up to 2	1
	Coking zone - - -	4 to 15	10
10	Superficial gas velocity, ft./sec.		
	Vaporization zone - - -	4 to 20	10
	Coking zone - - -	0.5 to 4	2
	Coke circulation ratio, lbs./lb. fresh feed		
15	From coking zone to vaporization zone - - -	1 to 50	24
	From coking zone to combustion zone - - -	1 to 10	3
20	From combustion zone to coking zone - - -	1 to 10	3
	Feed rate to vaporization zone, W/hr./W - - -	0.5 to 10	2.5
	% vaporized in vaporisation zone - - -	50 to 90	80
	1015° F.+conversion* - - -	70 to 100	100
25	*1015° F.+conversion is defined as:— 100 vol. % of fresh feed minus vol. % of products boiling above 1015° F., excluding coke.		

Table II illustrates the products obtainable from the feed stock indicated when the process of this invention is operated in accordance with the example of Table I.

TABLE II.

	Inspection on Hawkins Crude	
35	API Gravity - - -	26.2
	Conradson Carbon, wt. % - - -	7.5
	Sulphur, wt. % - - -	2.4
40	Viscosity, SSU @ 100° F. - - -	159
	SSU @ 130° F. - - -	108
	Products:— % based on feed	
45	C ₃ —gases - - -	3 wt. %
	C ₄ - - -	2 vol. %
	C ₅ —430° F. - - -	31 vol. %
	430°—1015° F. - - -	59 vol. %
	Gross coke make - - -	8 wt. %
50	Note:— All 1015° F.+material is recycled to extinction.	

Various alternative modes of operation will be apparent to those skilled in the art. For example, the upper or vaporization zone can

be operated at higher temperatures. This would allow some reduction in the coke circulation rate, or permit higher feed rates. The temperature in the vaporization zone can conveniently be used to adjust the endpoint of the heavy gas oil, beside the control obtained by recycling the heavy ends from the conversion products. One of the purposes for recycling these heavy ends is to return to the coker entrained coke particles not separated from the conversion products in cyclone 5. In some applications, it may be desired not to employ recycle operation; for example, when a heavy fuel oil product is desired. In such cases, the coke particles can be separated from the fuel oil as by settling or filtering, and the temperatures in the vaporization zone can be used as the endpoint control.

The process of this invention is admirably suited to the processing of highly aromatic oils such as Coleville crude, coal tars, cycle stocks and similar materials. With these types of oils, it is often desirable only to produce relatively low endpoint products as the high boiling products are of poor quality and of low value.

Having described the invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What we claim is:—

1. A process for converting hydrocarbon oils which comprises contacting an oil in an upper portion of a conversion zone with fluidized particulate substantially inert solids maintained at

a vaporization temperature in the range of 650° to 850° F. to vaporize a portion of said oil, removing overhead vapor and some solids with adhering unvaporized oil, separating vapors so created as product from the solids, conveying solids so separated along with adhering unvaporized portions of said oil to the lower portion of said conversion zone, maintaining in said lower portion fluidized particulate substantially inert solids at a coking temperature in the range of 900° to 1050° F. whereby said unvaporized portions are pyrolytically converted to gasiform conversion products and carbonaceous residue which is deposited on said solids, passing said conversion products upwardly through said upper portion to fluidize solids therein and to cool and condense the heavy ends from said conversion products, circulating stripped solids from said lower portion to said upper portion in an amount in the range of 1 to 50 lbs./lb. of said feed oil, circulating stripped solids from said lower portion to an external heating zone wherein they are reheated to a temperature 100° to 300° F. above said coking temperature, and returning solids so reheated to maintain said coking temperature.

2. The process of Claim 1 wherein the solids circulated to the upper portion are cooled.

30 3. The process of Claim 1 wherein said oil comprises a whole crude.

4. The process of Claim 1 wherein a portion of the reheated coke is mixed with the solids separated from said vapors immediately after the separation.

35 5. The process of Claim 1 wherein the vapors

removed as products are immediately quenched to a temperature below 600° F.

6. Apparatus for carrying out the conversion of hydrocarbons as claimed in Claim 1, which comprises, in combination, a vertically disposed vessel adapted to contain two fluidized beds of substantially catalytically inert particulate solids in the upper and lower portions thereof, said beds being in fluid communication by means of a gasiform distributing member located intermediate of said beds, means for establishing and maintaining fluidized beds of solids in the upper and lower portions of said vessel, means for introducing and distributing an oil into the upper fluidized bed, means for withdrawing and separating solids and gasiform products from said upper fluidized bed, conduit means for returning the solids so separated along with adhering non-vaporized portions of said oil to the lower fluidized bed, means for circulating stripped solids from said lower fluidized bed to the upper bed, and means for reheating the solids in said lower fluidized bed to maintain a coking temperature.

7. Apparatus of Claim 6 wherein said means for reheating the solids includes a transfer line burner wherein the solids circulated there-through are partially combusted.

8. Apparatus defined in Claim 6 comprising in addition thereto heat exchange means for cooling the stripped solids circulated from the lower to the upper fluidized bed.

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